UNIVERSITY OF PENNSYLVANIA

A DISTILLATION METHOD FOR THE DETERMINATION OF MERCURY IN ORGANIC COMPOUNDS AND A STUDY OF THE ACCURACY OF SEVERAL EXISTING METHODS FOR THE DETERMINATION OF MERCURY

EDWARD PUGH FENIMORE

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN

PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

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INTRODUCTION

In the new distillation method for the determination of mercury in organic compounds, described later, the sample is oxidatively decomposed by concentrated sulphuric acid and ammonium persulphate, in a special apparatus, and the mercury is distilled out as mercuric chloride by passing a current of hydrogen chloride and heating to about 310° C. The receiver, charged with a small volume of water, contains, after the distillation, considerable quantities of hydrochloric and sulphuric acids. Qualitative trials showed the anhydrous distillation of mercuric chloride, under the conditions outlined, to be rapid and complete, tests for mercury in the residual liquid in the distilling flask being negative. A method was sought for the determination of the mercury, present as mercuric chloride in a solution of about 60 cc. volume, containing considerable hydrochloric and sulphuric acids.

The nature of the solution at once excludes the thiocyanate titration, which within the somewhat limited range of its applicability is a very satisfactory rapid method for determination of mercury. There were tested in succession (1) the iodometric method of Rupp[1]; (2) determination as sulphide (a) by direct hydrogen sulphide precipitation, and (b) by Volhard's procedure; (3) precipitation of mercury as metal by excess stannous chloride (cf. Krieckhaus' method)[2], solution in nitric acid and titration with thiocyanate; and (4) the iodate method of Jamieson[3].

Critical trials of these methods revealed the fact that only the last possesses the requisite accuracy. This method was accordingly adapted to the conditions of the new distillation procedure, and is discussed later.

The failure of the sulphide method was unexpected, as this method enjoys a reputation for accuracy and is much used. The evidence obtained seems convincing, however, and is believed to be sufficiently important for somewhat detailed description. The results of the trials of the other methods will be presented more briefly.

The combination of the distillation procedure with the final determination of the mercury by Jamieson's method gave excellent results

when tested with inorganic mercury salts of known purity. In order to ascertain the accuracy of the method when applied to organic mercury compounds, it was considered advisable to adopt, for purposes of comparison, an "umpire method." This course seemed necessary because most of the organic mercury compounds available cannot be relied upon to contain the theoretical content of mercury, many cannot be purified in a really satisfactory manner, and in general can be tested as to purity only by analysis. Two methods were examined with respect to suitability as an umpire method: (1) the modified Eschka Method using a gold crucible[4] and (2) decomposition by concentrated sulphuric acid and solid potassium permanganate, followed by thiocyanate titration[5]. The second method was adopted for purposes of comparison, and is considered further in a later section.

The arrangement of material in this paper is as follows:

I. Tests of the Accuracy of Several Existing Methods for Determination of Mercury.
   (1) Determination as Mercuric Sulphide.
   (2) Iodometric Method of Rupp.
   (3) Isolation as Metal by Excess Reducing Agent, and Determination by Thiocyanate Titration.
   (4) The Iodate Method of Jamieson.
   (5) Selection of an Umpire Method for Comparative Purposes.

II. A Distillation Method for Determination of Mercury in Organic Compounds.

III. Conclusions.

I. Tests of the Accuracy and Suitability of Several Existing Methods for Determination of Mercury

The methods studied were several which seemed best adapted to the determination of mercury in a liquid such as that obtained in the distillation procedure described below. It was hoped that a volumetric method could be used, and it was confidently believed that if no volumetric procedure were found applicable, the mercury could be determined satisfactorily, even if not rapidly, as sulphide. The conditions imposed, i.e., the presence of rather large amounts of free hydrochloric and sulphuric acids, or of the salts formed by their neutralization, are not to be considered favorable to the accuracy of any method. In each case, however, the accuracy was tested first with simple solutions of pure mercury compounds before applying the method to solutions such as those obtained in the distillation procedure.

The mercury compounds used in the trials were two specimens of mercuric chloride and one of the oxide. Mercuric chloride No. 1 was the "C.P. Analyzed" salt twice recrystallized from water, only the middle fraction of crystals being taken; the purity is assumed to be practically 100%. Mercuric chloride No. 2 was the "C.P. Analyzed" salt once recrystallized from water containing hydrochloric acid. Its purity was found, by the Volhard method, to be 99.9%. The mercuric oxide was prepared by precipitation, using mercuric chloride and sodium hydroxide, washed until free of chloride, and dried over phosphorus pentoxide in a vacuum desiccator. Its purity was found to be 99.6%. The stated purity values were obtained as follows:

Determination of Purity of Mercuric Chloride No. 2 and of Precipitated Mercuric Oxide

The purity of this mercuric chloride was determined by precipitation of mercuric sulphide by the Volhard procedure applied to the solution containing at first nothing but the sample. The results were 99.94% and 99.85%, mean 99.90%.

The accuracy of the Volhard procedure as here applied was determined indirectly in the following way: A sample of the purified mercuric oxide was analyzed by the thiocyanate titration, the decinormal thiocyanate being standardized against carefully purified mercury metal, and under the same conditions of volume, acidity, etc., present in the analysis. The results for

purity were 99.59% and 99.56%, mean 99.58%. The same mercuric oxide was then analyzed by the Volhard method, the results being 99.49% and 99.61%, mean 99.55%. As under the conditions imposed, the analysis by thiocyanate titration could scarcely fail to be accurate, and the identity of the results by two methods so entirely different can hardly be a coincidence, it is concluded that the Volhard procedure, applied to a pure salt solution, is accurate. (As will appear later, it is not accurate under certain other conditions.)

These analyses also indicate the purity of the mercuric oxide to be very nearly 99.6%.

(1) *The Determination of Mercury as Sulphide.*

(a) *By Direct Precipitation with Hydrogen Sulphide*

The direct precipitation of mercury as mercuric sulphide from acid solution is a procedure the accuracy of which is apparently accepted as established[6]. The procedure is much used [5,7] and it is apparently assumed that the use of "the familiar sulphide method" places the chemist in a position that is analytically unassailable.

Tests of the direct precipitation of mercury as sulphide invariably yielded high results, a fact which was at first attributed, because of the confidence reposed in the accuracy of the method, to possible irregularity in the composition of the mercuric chloride. Continued work showed conclusively, however, that the sulphide obtained by direct precipitation is too heavy, that it is contaminated, e.g., with chlorine, and that this is apparently an inherent and perhaps ineradicable defect in the method.

Procedure—

The concentration of mercury was in no case allowed to exceed 0.1 gm. per 100 cc. (Treadwell[6]), and was generally less than this. The solution, in an Erlenmeyer flask, was acidified with 1 to 3 cc. of concentrated hydrochloric acid per 100 cc., and was saturated with hydrogen sulphide (under slight pressure) at room temperature. The precipitate was allowed to settle until the supernatant liquid was entirely clear. The liquid was decanted through a prepared Gooch crucible and the precipitate washed several times with cold water by decantation. The precipitate was then transferred to the filter and washed thoroughly with cold water, followed by alcohol and then ether.

The Gooch crucible was placed in a Wiley extraction apparatus and extracted from 1 to 2 hours with carbon disulphide. (A second extraction was repeatedly shown to be unnecessary.) Alcohol and then ether were passed through the crucible, which was then dried at 100°-105° C. and weighed.

The *Gooch crucibles* used in these tests were prepared with heavy mats of fine asbestos, and were provided with underlying discs of filter paper, as suggested by White[5]. This device is an aid to accuracy, crucibles so prepared coming almost at once to constant weight. It should be applicable in other analyses in which final high heating is not required, and seems to make unnecessary in such cases the rather elaborate preparation of the Gooch crucible described by Fales[5]. In the case of mercury sulphide, it affords further a safeguard against mechanical loss by penetration of the mat during carbon disulphide extraction.

Each Gooch crucible was prepared for use by passing through it a liquid as nearly as possible identical with that of the analysis, this operation being repeated until it was certain that the weight was constant within 0.0001 gram. The Gooch crucibles in all cases were dried for not less than an hour at 100°-105° C., kept for at least 30 minutes in a desiccator, then for 20-30 minutes in the balance case, and were then weighed to the nearest 0.00005 gram. The same weighing procedure was used in the analyses.

To avoid penetration of the Gooch mat during the extraction, due to continued dropping of carbon disulphide from a height of several inches, the crucible was covered with a disc of filter paper, with a narrow segment folded so as to form a shallow cone, into which the solvent dropped, passing through it into the crucible.

TABLE I

ANALYSES OF MERCURIC CHLORIDE AND MERCURIC OXIDE BY DIRECT PRECIPITATION WITH HYDROGEN SULPHIDE UNDER PRESSURE

Hg Compound	Sample gm.	Hg taken gm.	HgS gm.	Hg found gm.	Error gm.	Error %
$HgCl_2$ No. 1	0.49235	0.36378	0.42275	0.36449	+0.00071	+0.17
$HgCl_2$ No. 1	0.3002	0.2218	0.2577	0.2222	+0.0004	+0.18
$HgCl_2$ No. 1	0.3000	0.2216	0.2586	0.2230	+0.0014	+0.63
$HgCl_2$ No. 1	0.2999	0.2216	0.2581	0.2225	+0.0009	+0.41
$HgCl_2$ No. 2 (Purity 99.9%)	0.5001	0.3695	0.4294	0.3702	+0.0007	+0.20
$HgCl_2$ No. 2 (Purity 99.9%)	0.43665	0.3226	0.3756	0.32385	+0.0012	+0.38
HgO (Purity 99.6%)	0.3669	0.3384	0.3940	0.3397	+0.0013	+0.40
HgO (Purity 99.6%)	0.3937	0.3631	0.4227	0.3645	+0.0014	+0.37

As shown in the table, the errors were invariably positive, averaging 0.34%. To test the weighed residues of mercuric sulphide for contamination

by chlorine, several were in part removed from the Gooch crucibles, ground with lime, and ignited. The mass was taken up in dilute nitric acid, the liquid boiled free of hydrogen sulphide, filtered and precipitated with silver nitrate. The resulting silver chloride weighed 0.0098 gm. A blank experiment gave a turbidity barely detectable. There was accordingly shown a considerable contamination of the mercuric sulphide.

An effort was made to improve the results of the direct sulphide method by modification of the conditions of precipitation. In several trials, hydrogen sulphide was bubbled through the cold solution, which was then heated nearly to boiling, cooled, and again saturated with hydrogen sulphide; in others the mercury was precipitated from more dilute solution. Finally the dilute mercury solution was poured slowly and with stirring into an equal volume of saturated hydrogen sulphide water, in an attempt to obtain a precipitate of normal composition by having the hydrogen sulphide always in excess. The results of these trials are shown in Table II.

TABLE II

DIRECT PRECIPITATION OF MERCURIC SULPHIDE UNDER MODIFIED CONDITIONS
(Mercuric Chloride No. 1)

Conditions	Sample gm.	Hg taken gm.	HgS gm.	Hg found gm.	Error gm.	Error %
H_2S bubbled through cold solution; heated, cooled, and again saturated with H_2S	0.3011	0.2225	0.2596	0.2238	+0.0013	+0.58
	0.3028	0.2237	0.2608	0.2249	+0.0012	+0.54
Volume 400 cc.; Pressure-precipitation	0.1221	0.0902	0.1052	0.0907	+0.0005	+0.55
	0.1205	0.0890	0.1042	0.0898	+0.0008	+0.90
Sample in 200 cc. water added slowly to 200 cc. saturated H_2S water	0.3003	0.2219	0.2585	0.2229	+0.0010	+0.45
	0.3000	0.2216	0.2578	0.2223	+0.0007	+0.32

It will be noted that the changed conditions of precipitation entirely failed to remove, or even to diminish, the error.

Precipitation of Mercury as Sulphide from Sulphuric Acid Solution Containing Manganous Sulphate—A familiar method for the determination of mercury in organic compounds, described by White[5], involves decomposition of organic matter by suspending or dissolving the sample in concentrated sulphuric acid and adding powdered potassium permanganate in small portions. The mixture is diluted, oxides of manganese taken up with oxalic acid or hydrogen peroxide, and the mercury precipitated by hydrogen sulphide. The accuracy of the sulphide precipitation under these conditions was subjected to test.

Procedure—

In a 500 cc. Kjeldahl flask, 0.5 gm. pure sucrose was treated with 10 cc. concentrated sulphuric acid, and decomposed by adding to the warm mixture 1.5 gms. of powdered potassium permanganate in small portions. After cooling and diluting, the liquid was cleared with hydrogen peroxide solution, filtered, and added to a solution of a weighed sample of purified mercuric chloride (No. 2). The liquid was diluted to about 200 cc. and precipitated by hydrogen sulphide.

The results of these trials appear in Table III.

TABLE III

PRECIPITATION OF MERCURIC SULPHIDE FROM SULPHURIC ACID-MANGANOUS SULPHATE SOLUTION

(Mercuric Chloride No. 2—Purity 99.9%)

Sample gm.	Hg taken gm.	HgS gm.	Hg found gm.	Error gm.	Error %
0.1250	0.0923	0.10885	0.0939	+0.0016	+1.5
0.1882	0.1389	0.1632	0.1407	+0.0018	+1.1
0.1384	0.1022	0.12015	0.1036	+0.0014	+1.1
0.18225	0.1345	0.1572	0.1355	+0.0010	+0.6
					Average +1.1%

In White's method the positive sulphide error may be in part compensated by loss of mercury during the decomposition. Such loss was observed by White himself, the recovery being 98-99% of mercury taken as a pure salt.

In the experiments referred to in Table III, no loss could occur in this way, as the mercuric chloride sample was in no case present dur-

ing the addition of permanganate, the two solutions being mixed afterward. The positive error in the sulphide precipitation, under the conditions stated, may be assumed to stand fully revealed by these trials.

Precipitation of Mercury as Sulphide from Solutions of Double Iodide Containing Considerable Salts—In the analysis of iodine compounds by the distillation method described below, the iodine passes into the receiver together with considerable hydrochloric and sulphuric acids. It is necessary to add potassium iodide to bring mercuric iodide into solution, and the completion of the analysis, therefore, requires the determination of mercury in a solution of the double iodide containing considerable acid or the salts from its neutralization. Wegelius and Kilpi[9] reported precipitation of mercury sulphide to be incomplete in presence of excess iodide. This was confirmed for cases in which the acidity was high. However, when mercury sulphide was precipitated from slightly acid solutions of the double iodide containing the salts produced by the neutralization of the acidity just referred to, the results were much too high.

$HgCl_2$ gm.	Hg taken gm.	HgS gm.	Hg found gm.	Error gm.	Error %
0.1340	0.0980	0.1208	0.1042	+0.0053	+5.41
0.1632	0.1205	0.1470	0.1268	+0.0063	+5.23

An attempt to determine mercury in presence of iodide by a precipitation similar to that of Volhard, likewise gave high results.

The sample of mercuric chloride, in a solution containing 1 gm. potassium iodide and 25 cc. of 0.1N sodium hydroxide, was treated with hydrogen sulphide under slight pressure until the precipitate just redissolved. There was added 5 gms. of ammonium nitrate (as a filtered 50% solution) and the liquid was boiled to expel ammonia and to precipitate the mercury. Results:

$HgCl_2$ gm.	Hg taken gm.	HgS gm.	Hg found gm.	Error gm.	Error %
0.3062	0.2262	0.2644	0.2280	+0.0018	+0.80
0.3008	0.2223	0.2585	0.2229	+0.0006	+0.27

(b) *Determination of Mercury, Present as Double Iodide in Solution Rich in Salts, by Double Precipitation of the Sulphide*

In a final effort to make satisfactory application of the sulphide determination to solutions of mercury containing iodide, the mercury was first precipitated by hydrogen sulphide, the precipitate dissolved in sodium sulphide reagent, and the sulphide again precipitated by ammonium nitrate, as in Volhard's method. A similar procedure was applied by Pretzfeld[10], who obtained thereby results "somewhat high, the error being about 1.2% of the amount taken." In these experiments iodide was absent, ammonium chloride was used for the second precipitation, the mercury sulphide was collected, washed twice with carbon disulphide and weighed on counterpoised papers. Pretzfeld attributed the positive error to presence of sulphur, but reported no attempt to test the point. Since the presence of sulphur in Pretzfeld's precipitate was not excluded, there seemed to remain the possibility that by a similar double precipitation, followed by more efficient carbon disulphide extraction, mercury sulphide precipitates of improved or normal composition could be obtained, even from iodide solution rich in salts.

A solution containing 5 cc. concentrated sulphuric acid and 10 cc. concentrated hydrochloric acid was neutralized with sodium hydroxide, filtered, and added to a solution of the sample of mercuric chloride. There was introduced 10 cc. of 10% potassium iodide; the solution was diluted to about 200 cc. and saturated with hydrogen sulphide. The precipitate was collected on a filtering crucible with porous porcelain bottom, washed with water, and then dissolved in 20 cc. of hot sodium sulphide solution (10% $Na_2S.9H_2O$, 5% NaOH). A gray stain remained on the filtering surface and was not removable by the reagent. The filtrate was diluted to 150-200 cc., treated with 5 grams of ammonium nitrate (added as a filtered 50% solution), and boiled gently until ammonia-free. The precipitate was collected, washed, and extracted with carbon disulphide as usual. Results:

$HgCl_2$ gm.	Hg taken gm.	HgS gm.	Hg found gm.	Error gm.	Error %
0.12775	0.0943	0.1141	0.0984	+0.0041	+4.35
0.1520	0.1122	0.1347	0.1161	+0.0039	+3.48

The failure to effect the desired improvement by double precipitation is thought to be due to the relatively large amount of sodium sulphide required to dissolve the filtered mercuric sulphide. As a result the Volhard precipitation is made in presence of a considerable quantity of salts, and the sulphide is contaminated.

Conclusions—

The results reported above indicate that the determination of mercury as sulphide by direct precipitation with hydrogen sulphide is affected by a positive error of more than permissible magnitude. With simple solutions of mercuric salt and hydrochloric acid, the errors averaged +0.34% (Table I) and were not diminished by modifications in procedure (Table II). Under less favorable conditions (in presence of iodide and neutral salts; of sulphuric acid and manganous sulphate) the errors were larger (Table III). Conditions could not be found under which direct precipitation of mercuric sulphide by hydrogen sulphide yielded results sufficiently accurate for good analytical work.

Re-solution of mercuric sulphide (precipitated from a solution containing iodide and considerable salts) in sodium sulphide and reprecipitation by ammonium nitrate gave results scarcely better than those obtained by direct precipitation under the same initial conditions.

Volhard's method, applied to solutions containing only a mercuric salt, gave accurate results. In presence of other salts in considerable amount, and of iodide, the sulphide obtained was too heavy. At what concentration of other salts this error becomes appreciable should be determined in order to establish the status of the Volhard procedure as a general method.

Discussion—

While no proved explanation can be offered to account for the excessive weight of precipitates of mercuric sulphide obtained as described above, there is available a certain amount of information which is at least suggestive.

Rose[11] in 1822 prepared the compound $HgCl_2.2HgS$ by interaction of mercuric chloride and freshly precipitated mercuric sulphide.

Qualitative tests made under the direction of Dr. J. H. Müller (privately communicated) showed that freshly precipitated and well-washed mercuric sulphide, when shaken with a solution of mercuric chloride, nitrate, sulphate or acetate, can remove all the mercury from solution. Furthermore, it is well known that during the early stages of precipitation of mercuric sulphide by hydrogen sulphide, there are formed white or colored insoluble "compounds" of the general type $mHgA_2.nHgS$, illustrated by the white compound $HgCl_2.2HgS$. If intermediate compounds of the chlorosulphide type are not quantitatively transposed to HgS, the final precipitate will contain the anion present, e.g., chlorine, and will be too heavy. It will be recalled that several mercuric sulphide precipitates (whose weights were too great) were examined for halogen, which was found to be present, not in traces but in amounts sufficient to constitute a real contamination.

The ability of mercuric salts to unite additively with molecules possessing active or latent unsaturation is recognized as a characteristic property. It is illustrated by the cases already mentioned, and also by the union of mercuric salts with olefinic compounds[12], with acetylene[13], with acetone[14] and with thio-ethers, etc.

Smith and Semon[15], in a research dealing in part with the formation of intermediate compounds during the precipitation of certain metals (especially mercury) by hydrogen sulphide, reached conclusions which seem to admit the possibility of errors in the determination of mercury as sulphide. The mechanism of the precipitation of mercuric sulphide (by hydrosulphide ion; cf. Stieglitz[16]) is indicated as follows, the addition-compounds being represented as co-ordinated complexes:

$$2\ HgX_2 + 2\ H^{+}, SH^{-} \longleftrightarrow \left[\begin{array}{c} S\text{–}H \\ Hg \diamond Hg \\ S\text{–}H \end{array}\right] X_2 + 2\ HX$$

I

$$\left[\begin{array}{c} S\text{–}H \\ Hg \diamond Hg \\ S\text{–}H \end{array}\right] X_2 \longleftrightarrow [Hg\text{-}S\text{-}Hg]X_2 + H_2S$$

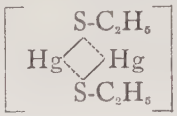
II

$$2\ [\text{Hg-S-Hg}]X_2 \longleftrightarrow \underset{\text{III}}{[\text{Hg}(\text{SHg})_2]X_2} + \text{HgX}_2$$

$$[\text{Hg}(\text{SHg})_2]X_2 + 2\ \text{H}_2\text{S} \longleftrightarrow [\text{Hg}(\text{SHg})_2](\text{SH})_2 + 2\ \text{HX}$$

$$[\text{Hg}(\text{SHg})_2](\text{SH})_2 \longleftrightarrow [\text{Hg}(\text{SHg})_2]\text{S} + \underset{(\text{i.e. } 3\ \text{HgS})}{\text{H}_2\text{S}}$$

Compound I was not isolated, but the type is represented by the analogous mercaptido complex—



such as the perchlorate made by action of mercaptan upon a solution of mercuric perchlorate. Loss of H_2S from I is to be expected, and would yield a compound of formula II. The existence of this compound was inferred from the fact that on treating mercuric sulphide with an exact equivalent of mercuric perchlorate, the sulphide just redissolved: $HgS + Hg(ClO_4)_2 \rightarrow [HgSHg]\ (ClO_4)_2$. When this solution was allowed to stand there separated slowly a white insoluble compound corresponding to formula III, viz., $[Hg\ (SHg)_2]\ (ClO_4)_2$ or $Hg(ClO_4)_2.2HgS$. This product was isolated and analyzed. It was prepared also by the method of Rose. It was found to dissociate slightly in water, yielding some HgS, and to be convertible to HgS by hydrogen sulphide.

For further experimental details and discussion, the original paper should be consulted.

Examination of the above mechanism shows that five reactions must go to completion in order to obtain pure mercuric sulphide. Compound III is sparingly soluble, and its decomposition according to the fourth (and fifth) equations might be incomplete. The ability of freshly precipitated mercuric sulphide to carry down other substances, referred to previously, would lead to high results if there were thus co-precipitated compound III, compound II, or the original mercury salt.

The mechanism given could equally well be used to explain incomplete precipitation of mercury by hydrogen sulphide (if this were to occur), since compounds I and II are soluble, and since formation of compound III returns to the solution one-fourth the mercury hitherto involved. The facts of analy-

sis, however, seem to exclude a considerable operation of any irregularity leading to low results.

The high results obtained when mercury is precipitated by Volhard's method in presence of salts are probably not due to complicated intermediate reactions, such as those shown above for precipitation by the hydrosulphide ion. In the case of this method, therefore, positive errors are probably due to co-precipitation of other salts with mercuric sulphide, as a result of adsorption or chemic union.

(2) *Iodometric Method of Rupp*

In the method proposed in 1906 by Rupp[1], the alkaline solution containing mercury as double iodide is treated with formaldehyde, the mercury separating as metal. The slightly acidified liquid is now treated with a measured excess of standard iodine solution, and is shaken until all the mercury has dissolved. The excess iodine is titrated with thiosulphate.

The method has been the subject of some discussion and criticism[17]. It was improved by Kolthoff[18] by use of barium hydroxide and hydrogen peroxide for the reduction. This modification could, of course, not be applied in the present work, and the method was accordingly tested in the form described by Rupp. Results of some trials made with pure mercuric chloride are listed below. The iodine solution was standardized against the thiosulphate, and the latter against potassium iodate.

TABLE IV

ANALYSES OF MERCURIC CHLORIDE NO. 1 BY RUPP'S IODOMETRIC METHOD

Sample gm.	Hg present gm.	Hg found gm.	Error gm.	Error %
0.4000	0.2955	0.2975	+0.0020	+0.48
0.4001	0.2956	0.2973	+0.0017	+0.42
0.3999	0.2954	0.2969	+0.0015	+0.38
0.4001	0.2956	0.2975	+0.0019	+0.47
0.4002	0.2957	0.2977	+0.0020	+0.50

The results are sufficiently concordant, but average 0.45% too high. The method is somewhat less convenient than appears, due to the prolonged shaking of the liquid sometimes required to dissolve the mercury.

(3) *Isolation of Mercury as Metal and Determination by Thiocyanate Titration*

Mercury obtained as chloride in the distillation procedure cannot be determined by direct titration with thiocyanate. To exclude this interference of halogen, trials were made of several methods by which the mercury may be precipitated as metal, separated mechanically, dissolved in nitric acid, and titrated with thiocyanate.

Reduction by Stannous Chloride.—Precipitation of mercury as metal by reduction with stannous chloride, followed by separation of the mercury by decantation and its determination by weighing, was reported by Fresenius[1] to yield results more than 1% low, due to mechanical loss during decantation. Krieckhaus[2] uses the decantation procedure, dissolves the isolated mercury in nitric acid and titrates it with thiocyanate. In order to exclude loss of mercury during the decantation, the method of Krieckhaus was modified by decanting through a filter to retain any floating particles of mercury. The procedure used in trials of the method is outlined below.

The acidified mercury solution having a volume of 75 cc. is treated in an Erlenmeyer flask with 60 cc. of stannous chloride reagent (50 gms. stannous chloride in 50 cc. concentrated hydrochloric acid, with 150 cc. water added last). The reagent is added at first by drops until the precipitated mercurous chloride begins to darken, when the remainder is added more rapidly. The mixture is warmed on the water-bath for 30 minutes to hasten the coalescence of the mercury particles into globules. The liquid is decanted through a filter, the mercury being retained as completely as possible in the flask, which is then rinsed out with water containing sulphuric acid. Flask and filter are washed until the washings are chlorine-free. The filter paper is transferred to the flask, 10 cc. of concentrated nitric acid added, and mercury dissolved, and the paper disintegrated by heating until oxides of nitrogen are expelled. The liquid is cooled, diluted to 20 cc. and treated with permanganate solution to permanent pink. Excess permanganate is reduced by careful addition of dilute hydrogen peroxide, 5 cc. of saturated ferric alum solution added, and the volume made up to 30 cc. The mercury is titrated with 0.1N potassium thiocyanate, standardized against pure mercury. Results are given in Table V.

TABLE V
MODIFIED METHOD OF KRIECKHAUS

$HgCl_2$ gm.	Hg taken gm.	Hg found gm.	Error gm.	Reduction
0.4223	0.3117	0.3114	–0.0003	cold; overnight
0.3333	0.2460	0.2458	–0.0002	cold; ½ hour
0.3160	0.2333	0.2330	–0.0003	cold; ½ hour
0.39505	0.2916	0.2913	–0.0003	hot
0.3976	0.2935	0.2934	–0.0002	hot
0.1880	0.1389	0.1384	–0.0005	cold; ½ hour
stock solution	0.10025	0.0996	–0.00065	cold; ½ hour
stock solution	0.10025	0.0997	–0.00055	cold; ½ hour
stock solution	0.10025	0.0998	–0.00045	cold; ½ hour
stock solution	0.10025	0.0999	–0.00035	cold overnight, then heated
0.09995	0.0738	0.0726	–0.0012	cold; 3 hours
0.0972	0.0717	0.0709	–0.0008	cold; ½ hour
0.08375	0.0618	0.0610	–0.0008	hot
0.0715	0.0528	0.0515	–0.0013	cold; ½ hour
stock solution	0.0401	0.0395	–0.0006	cold; overnight
stock solution	0.0401	0.0394	–0.0007	cold; overnight then heated

For quantities of mercury not less than 0.2 gm., the method gives satisfactory results. With samples of about 0.1 gm., the results are barely acceptable, and with smaller samples the results are considerably too low.

When the stannous chloride reduction was applied to mercuric chloride in solutions such as those obtained in the distillation method described in Section II, the mercury separated more finely divided, and in several cases passed in part through the filter. In spite of the satisfactory character of the method from a manipulative standpoint, it was accordingly judged unsuited to the purpose.

Reduction by formaldehyde (as in Rupp's method) yielded finely divided precipitates of mercury and the results obtained were much too low.

Reduction by zinc.—By a procedure similar to that of Francois[20], the zinc being dissolved from the amalgam by prolonged action of

6N hydrochloric acid, it was found impossible to obtain a chlorine-free globule of mercury. The thiocyanate titration always gave low results, and the gravimetric method used by Francois was considered to be too tedious.

(4) *Iodate Method of Jamieson*[8]

The neutral or somewhat acid solution of mercuric salt is treated with a zinc sulphate-ammonium thiocyanate reagent, which precipitates white zinc mercuric thiocyanate, $ZnHg(SCN)_4$. This is removed by filtration, suitably washed, treated with excess hydrochloric acid and titrated with a standard solution of potassium iodate, the following reaction taking place:

$$ZnHg(SCN)_4 + 6\ KIO_3 + 12\ HCl \rightarrow HgSO_4 + ZnSO_4 + 2\ H_2SO_4 + 6\ ICl + 4\ HCN + 6\ KCl + 2\ H_2O$$

A similar titration is more familiar for the determination of copper[21].

The analytic advantage resulting from the ratio $Hg \simeq 6\ KIO_3$ is pronounced. Jamieson observed that excess of ammonium salts has a retarding effect upon the precipitation, hence it was thought better to use potassium (rather than ammonium) thiocyanate in the precipitating reagent. Otherwise, the original method was used unchanged for some preliminary trials, the results being quite satisfactory (Table VI, A). Some experimental trials were then conducted to find what modifications would be required to permit application of the method to the mercury solution obtained in the distillation procedure of Section II (volume 80-100 cc.; salts formed by neutralization of hydrochloric and sulphuric acids present). The course of this work can be seen by examination of Table VI, C & D.

Details of Jamieson's procedure are given as part of the distillation method, on page 31, and will be omitted here.

The results shown in Table VI appear to justify these conclusions:

A—The original method, applied to a simple acidified solution of mercuric salt, is accurate.

B—The precipitate should be washed from 5 to 10 times with the 1:100 precipitant. Excessive washing with this liquid leads to loss, due to solubility of the precipitate. Washing even once with water or dilute $ZnSO_4$ solution causes distinct loss.

Table VI

Determination of Mercury by Jamieson's Iodate Method

Method	Reagent* cc.	Time of P'ptation Hrs.	Total Vol. Liquids cc.	Washings**	Hg taken gm.	Hg found gm.	Error gm.
A—*Jamieson's Method Unchanged*	25	2	75	5	0.0742	0.0743	+0.0001
	"	"	"	"	"	0.0744	+0.0002
	"	"	"	"	"	0.0743	+0.0001
Solution acidified with 5 cc. HCl	"	"	"	6	"	0.0743	+0.0001
More precipitant	35	"	"	"	"	0.0749	+0.0007
B—*Washing Experiments*	25	2	75	10	0.0742	0.0742	0.0000
	"	"	"	"	"	0.0742	0.0000
	"	"	"	20	"	0.0737	−0.0005
Final washing with cold water	"	"	"	5	0.0785	0.0781	−0.0004
	"	"	"	"	0.0742	0.0738	−0.0004
	"	"	"	"	0.0742	0.0737	−0.0005
Final washing with 1% $ZnSO_4$	"	"	"	"	0.0798	0.0789	−0.0009
C—*Trials to Determine Conditions for Precipitation in presence of salts as in Distillation Method*	25	2	75	5	0.0742	0.0740	−0.0002
	"	"	"	10	"	0.0737	−0.0005
	35	"	85	10	"	0.0743	+0.0001
	50	"	150	10	"	0.0726	−0.0016
Solution contained salts from neutralization, 5 cc. H_2SO_4 and 10 cc. HCl by NaOH; acidified with 5 cc. HCl	25 of 2 x conc.	"	125	10	"	0.0736	−0.0006
	50 of 2 x conc.	"	200	5	"	0.0728	−0.0014
	25 of 2.5 x conc.	"	125	5	"	0.0744	+0.0002
	"	"	"	6	"	0.0738	−0.0004
	"	"	145	6	"	0.0744	+0.0002
D—*Trials by Best Conditions* Total volume 125 cc.; 25 cc. reagent of 2.5 x conc.; 1 cc. excess HCl; salts as in C.	25 of 2.5 x conc.	1	125	5	0.0742	0.0743	+0.0001
	"	"	"	"	"	0.0737	−0.0005
	"	"	"	"	"	0.0742	0.0000
	"	"	"	"	"	0.0739	−0.0003
	"	"	"	"	"	0.0745	+0.0003
	"	"	"	"	"	0.0745	+0.0003
E—*Tests of Time Required for Precipitation* (Conditions as in D)	"	3	"	6	0.0742	0.0742	0.0000
	"	2	"	10	"	0.0741	−0.0001
	"	1½	"	6	"	0.0742	0.0000
	"	¾	"	8	"	0.0742	0.0000
	"	½	"	5	"	0.0743	+0.0001
	"	¼	"	6	"	0.0742	0.0000

* KSCN 50 gms.
$ZnSO_4 7H_2O$ 29 gms. } per litre

** 5 cc. reagent in 450 cc. H_2O

C, D—Complete precipitation in presence of a considerable concentration of salts (NaCl, Na_2SO_4) requires increase in the quantity of precipitant. A considerable increase in the amount of precipitant is required for complete precipitation from larger volumes.

E—In presence of neutral salts in considerable amount, and by use of a large quantity of precipitant, complete precipitation is remarkably rapid, even 15 minutes being sufficient.

The method of Jamieson, with the modifications indicated in Section D of Table VI, was adopted for determination of mercury obtained from organic compounds by the distillation procedure. Considerable experience with the method showed that precipitation is not always complete in the shorter intervals indicated in Section E of the Table, and accordingly a period of 1 hour or longer is specified as preferable.

(5) *Selection of an "Umpire Method" for Comparative Purposes*

To provide a basis for comparison of the results obtained by the new distillation method, described later, there was sought a reliable and fairly rapid "umpire method" for determination of mercury in organic matter. Decomposition in a closed tube by fuming nitric acid, as in the Carius method[22], possesses the usual disadvantages of this rather cumbersome procedure. Determination of mercury as metal by the classical lime method, or one of its numerous modifications, offers the advantage of directness but not of convenience and rapidity. The highest development of the original procedure was effected by Bouton and Duschak[23], who distilled out mercury disengaged by ignition with lime, dissolved the mercury in nitric acid and titrated with thiocyanate. Their procedure is intended specifically for determination of mercury in minerals, but it succeeds in presence of small amounts of organic matter, and could perhaps be extended so as to permit satisfactory determination of mercury in organic compounds. The method of Eschka[24], in the modification presented by Whitmore[4], appeared to possess the requisite qualifications and was tested.

In the *method of Whitmore* the apparatus consists of an iron decomposition crucible and above it an inverted gold collecting crucible, both with flanges which are bound together tightly during the analysis by two steel

rings held by machine screws. Decomposition is effected by heating with mixtures of sodium carbonate and barium peroxide, barium or calcium carbonate, etc., or with Eschka's mixture, and the mercury which amalgamates on the gold crucible is weighed. The method is said to be generally satisfactory, even for compounds containing iodine.

The method was used in the analysis of a specimen of mercurated dibromofluorescein shown (by White's method) to contain 27.77% mercury. Of seven analyses using the gold crucible, one was lost by spattering of the charge, and one by obviously incomplete decomposition. Decomposition was apparently not wholly complete in several other trials (the charge having finally a pink tinge), and some doubt was thrown on every analysis by appearance of mercury on the flange. Results of the six completed analyses follow: 27.47, 27.41, 27.81, 26.90, 27.00, 27.86% mercury. Only the third and last are acceptable, and both analyses were visibly faulty in the ways mentioned. It was concluded that the method requires considerable practice, the proper adjustment of the heat being apparently important. Escape of traces of mercury between the flanges seems to be favored by the design of the apparatus, there being no provision for the escape of water, etc., formed in the decomposition.

The *method of White*[5] involves decomposition of the sample in warm concentrated sulphuric acid by addition of powdered potassium permanganate. Oxide of manganese is dissolved by addition of oxalic acid or hydrogen peroxide, and the mercury is determined in the diluted solution by precipitation with hydrogen sulphide or, in absence of halogen, by thiocyanate titration. Determination as sulphide was excluded for reasons already given. Trials of White's method, using the thiocyanate titration, showed it to be satisfactory, and it was adopted as a comparison method. The procedure follows:

Determination of Mercury in Organic Compounds by Decomposition with Potassium Permanganate and Sulphuric Acid and Titration of Mercury with Thiocyanate [5,25].

(Applicable only in absence of halogen; all reagents must be halogen-free).

White's directions were followed with little modification:

The sample, in a small glass weighing cup, was introduced into a 500 cc. Kjeldahl flask, and mixed with 10 cc. of concentrated sulphuric acid. The acid was heated gently (about 50° C.) and powdered potassium permanganate was added slowly in very small portions, with rotation of the flask after each addition. The temperature was raised somewhat as the decomposition proceeded, in order to keep the mixture suitably fluid, but decompositions were in all cases effected satisfactorily without the frequent flashes of flame which it is difficult to avoid when the acid is very hot. [The higher temperatures

at first specified were afterward found also by White (private communication, 1926) to be inadvisable]. When the mixture temporarily retained the color of the oxidant, about 0.2 gm. more of permanganate was added, the color being finally dark brown. The quantity of permanganate required varied with the weight and identity of the sample, but the 1 to 1.5 gram specified by White was generally sufficient.

The cooled mixture was diluted with about 25 cc. of water, and oxide of manganese *nearly all* dissolved by addition of a saturated solution of oxalic acid to the warm liquid, which was then transferred to a 250 cc. Erlenmeyer flask. The liquid was cooled, decolorization completed by cautious addition of dilute hydrogen peroxide, 5 cc. of 40% ferric alum indicator added, and the solution diluted to 100 cc. (± 5 cc.). The mercury was titrated with 0.1N potassium thiocyanate, the flask being agitated and chilled near the end of the titration to cause separation of mercuric thiocyanate, presence of which in suspension improves the end-point.

The *thiocyanate solution* was standardized against pure metallic mercury. The weighed globule was dissolved in 1 cc. of concentrated nitric acid in a 250 cc. Erlenmeyer flask, with cautious heating to oxidize mercury and to expel most of the oxides of nitrogen. The solution was diluted to about 50 cc., oxidized with permanganate solution, treated with 10 cc. of concentrated sulphuric acid, and cooled. It was decolorized carefully with dilute hydrogen peroxide, treated with 5 cc. of ferric alum indicator, diluted to 100 cc., and titrated with the thiocyanate.

The conditions in this standardization duplicate in essential features those of the analysis. Standardization in a solution containing 10 cc. nitric acid in an initial volume of 30 cc. gave higher normalities.

White's reported losses (1-2% of the mercury taken; see page 11) may actually have been greater if mercury was determined as sulphide. Trials were accordingly made to test possible loss of mercury during the decomposition. There were used weighed samples of mercuric acetate whose purity was shown, by direct thiocyanate titration, to be 99.98% (62.93% and 62.95% mercury; theoretical 62.95%). To provide oxidizable matter, 0.2 gram of sucrose was added, and the decomposition was effected as outlined above, using 1 gram of potassium permanganate. Results are shown in Table VII.

It is shown that serious loss of mercury is possible, but not inevitable, when the temperature used is rather high, the effect being no doubt dependent upon the results of single additions of permanganate and hence somewhat variable. By decomposition at relatively low temperature, however, loss of mercury may be avoided or kept within the permissible error of analysis.

TABLE VII

TESTS OF LOSS OF MERCURY DURING POTASSIUM PERMANGANATE-SULPHURIC ACID DECOMPOSITION

Conditions	Sample gm.	Hg present %	Hg found %	Error %
Decomposition at	0.33945	62.94	62.84	−0.10
low temperature;	0.3089	62.94	62.93	−0.01
some carbon left unoxidized	0.3097	62.94	62.93	−0.01
Higher temperatures,	0.3125	62.94	62.27	−0.67
with several	0.3017	62.94	62.97	+0.03
flashes	0.3141	62.94	62.02	−0.92

The error of White's method, when mercury is determined by titration (and not as sulphide), is likely to be negative. Though such error is perhaps rather often present, the results are satisfactory when the decomposition is properly effected. This fact, together with the rapidity and simplicity of the procedure, led to its adoption as a comparison method. Results obtained by it with various types of organic mercury compounds are listed later (Table VIII) in comparison with results by the distillation procedure, the former being generally slightly lower.

The usefulness of the umpire method described is much restricted by its inapplicability to compounds containing halogen, presence of which both increases the likelihood of loss of mercury during the decomposition, and excludes entirely the convenient thiocyanate titration. To permit satisfactory tests of the distillation procedure described in Section II, with respect to its applicability to halogen-containing compounds, the following device was used: A halogen-free organic mercury compound, analyzable by the umpire method, was mixed with mercury-free organic compounds of bromine and iodine, and the mercury determined by the distillation method. Results of these trials appear in Table VIII.

II. A Distillation Method for Determination of Mercury in Organic Compounds

During the analysis of mercurated dibromofluorescein by Robertson's chromic acid method[26] some mercury was observed to leave the decomposition flask as mercuric bromide, making impossible the proposed determination of both mercury and bromine in the same sample. This behavior of mercuric bromide led to the suggestion that the mercury obtained from organic compounds by a similar decomposition might be distilled quantitatively, as the more volatile chloride, by use of hydrogen chloride and a temperature near the boiling-point of mercuric chloride.

The distillation of metals as anhydrous chlorides is familiar in the analysis of certain minerals which are advantageously decomposed by heating in a stream of chlorine, carbon tetrachloride, etc., and similar procedures have been employed to effect separations of metals. The wet distillation of certain metals as chlorides, to separate them from other metals whose chlorides are not volatile with steam, is exemplified by the case of arsenic. This was distilled as the trichloride, in toxicological analysis, by Schneider[27] and by Fyse[28] in 1851. The method has been modified and improved by E. Fischer[29], Hufschmidt[30], Rohmer[31], Roark and McDonnell[32] and others. Fischer applied the method to the separation of arsenic from antimony, tin and also from mercury. Strecker[33] separated arsenic, antimony and tin from other metals of the second group, but found that during the distillation of antimony some mercury also passed over. Strecker and Conradt[34] took advantage of the volatility of mercuric chloride in steam containing hydrochloric and hydrobromic acids to separate mercury from metals forming non-volatile chlorides (Cu, Pb, Cd, Fe, Ba).

It seems proper, because of the superficial similarity of the last-mentioned method and the distillation procedure described in this paper, to point out at once their substantial and important differences.

The distillation methods referred to above were devised primarily as means for separation of certain metal chlorides in analyzable condition. A method for determination of arsenic in organic compounds, by distillation as the trichloride, was worked out by Rupp and

Lehmann[35]. The distillation method has not hitherto been employed for the determination of mercury in organic compounds.

In the method of Strecker and Conradt, the mercuric chloride is distilled in the presence of water, and is actually transferred from the flask by steam-distillation, assisted by hydrochloric and hydrobromic acids. The highest temperatures used by Strecker and Conradt were about 180° C.; no attempt was made to conduct the distillation under anhydrous conditions, nor to remove the mercuric chloride by distillation at or near its boiling-point. The presence of water in all these procedures greatly retards the distillation of mercuric (or other) chloride, the required time varying from about 1 to 4 hours. There is also the further disadvantage that the mercury chloride is obtained finally in a fairly large volume of distillate containing much hydrochloric (or hydrobromic) acid, practically requiring the determination of the mercury as sulphide under conditions certain to yield high results.

In the new distillation method, the sample is decomposed by ammonium persulphate and concentrated sulphuric acid. A stream of dry hydrogen chloride is then introduced and the temperature is raised rapidly to 305°-310° C. The mercury chloride distills out completely and rapidly, this operation requiring only a few minutes, and is obtained finally in a volume of about 60 cc. containing considerable acid. After neutralization, the method of Jamieson can be applied directly (except in presence of iodine) to the determination of the mercury.

The Distillation Method

Apparatus—

The final form of the complete apparatus is shown in the figure.

Reagents—

Potassium bisulphate-sulphuric acid mixture[36]

A mixture of 45 parts by weight of salt and 55 parts of concentrated acid, heated to 320° C. until boiling ceases.

Jamieson's Reagent

A—(Required only for compounds which contain iodine). A filtered solution of 29 grams $ZnSO_4.7H_2O$ and 50 grams KSCN per litre.

B—Modified Reagent (For use in absence of iodine). A solution of 2½ times the above strength; 73 grams $ZnSO_4.7H_2O$ and 125 grams KSCN per litre.

Wash-liquid

5 cc. of reagent A, or 2 cc. of reagent B, in 450 cc. of water, in a wash-bottle.

Standard Potassium Iodate Solution

19.2025 grams of pure KIO_3 per litre. This solution has almost exactly the theoretical oxidizing value (1 cc. $\simeq$ 0.0030 gram mercury). Small variations were observed, however, in results obtained by different analysts, and consequently the iodate solution was *empirically standardized against pure mercuric chloride* by that form of Jamieson's method to be used in the analysis (page 30 or page 32). Since the method is probably not altogether free from a personal factor, this procedure in general increases the certainty of accuracy in the analysis.

Hydrochloric Acid (for titration)

A cold mixture of 350 cc. concentrated hydrochloric acid and 100 cc. water.

Sodium Hydroxide, saturated aqueous solution

Ammonium Persulphate, granular

Fuming Sulphuric Acid (10%)

Zinc Dust (required in analysis of iodine compounds).

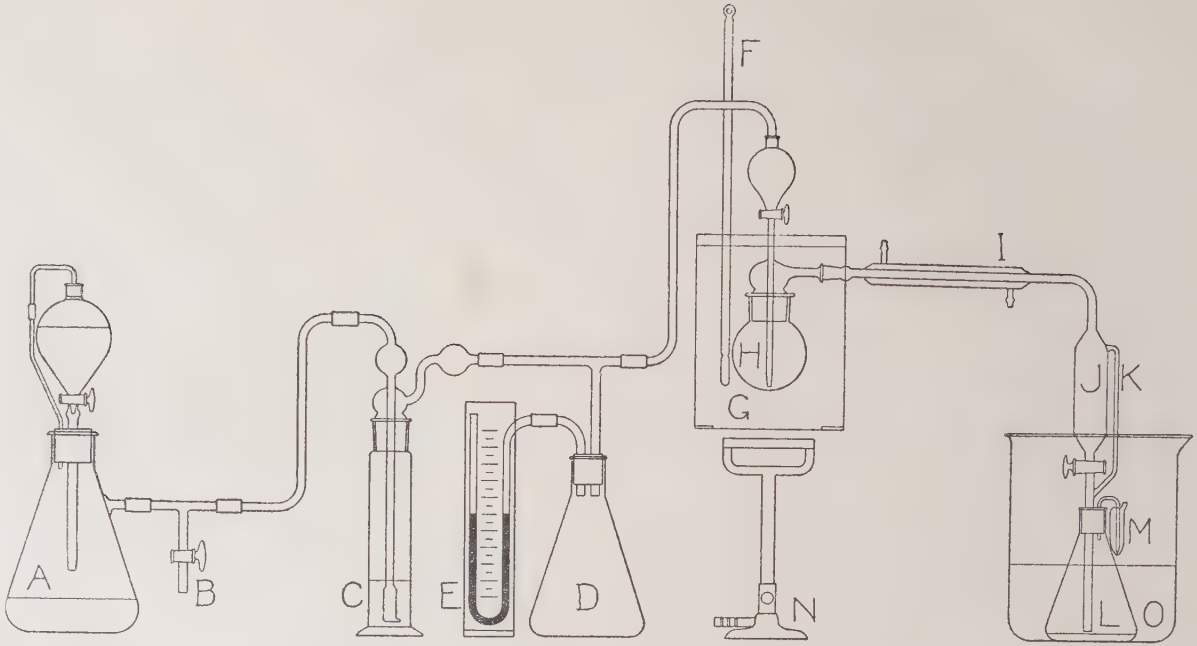
Other required chemicals are those ordinarily at hand. All chemicals used were of the best analytical grade.

Procedure—

(1) *Decomposition of Sample and Distillation of Mercuric Chloride*

The sample, containing not over 0.15 gram of mercury, is weighed in a small glass cup, and introduced into the decomposition flask H. The sample is dissolved in the least amount (5 cc. or less) of fuming sulphuric acid, with gentle warming if necessary. There is then added 20 cc. of the bisulphate-sulphuric acid solution (to mitigate the oxidation, and to raise the boiling-point of the mixture), and the contents of the flask are mixed by rotation. To the cool mixture is added 10 grams of ammonium persulphate and the flask is connected to the condenser and receiver, the latter containing 15 cc. water and the trap about 5 cc.

The flask is cautiously heated until the reaction starts, after which the oxidation generally proceeds to completion without further application of heat. In some cases moderation of the action by external cooling is necessary. During the decomposition it is advantageous to move the flask back and forth so as to keep its contents well mixed. When this is done, 10 grams of persulphate should be ample for the oxidation. Decomposition by persulphate is unusually smooth and rapid, and the residue entirely colorless. When oxidation is complete, heat is applied to decompose excess persulphate and to remove water formed in the oxidation.



A—HCl generator
B—Pressure release
C—H_2SO_4 dryer and bubble counter
D—Safety flask
E—Manometer

F—Thermometer
G—Air bath
H—Decomposition flask and still, 125 cc.
I—Condenser
J—Distillate reservoir—capacity 7 cc.

K—Vapor by-pass
L—Receiver—capacity 125 cc.
M—Trap
N—Ring burner
O—Cooling bath

The flask is cooled to about 100°-150° C., and the receiver is surrounded with cold water or with ice and water. The hydrogen chloride generator is connected with the flask, and the metal air-bath placed in position, as shown in the figure. A slow stream of hydrogen chloride is passed through the system, while the temperature is raised, during about 10 minutes, to 305°-310° C. The mercuric chloride begins to distill out considerably below 300° C., and around this temperature passes over very rapidly, collecting at first in the outlet tube and condenser. The temperature is maintained around 305°-310° C. for about 5 minutes, during which time some sulphuric acid distills over, collecting in the chamber J. The apparatus is allowed to cool, after which the stream of hydrogen chloride is discontinued, and the receiving unit of the apparatus is disconnected at P. The collecting chamber J now contains most of the mercuric chloride, and about 5 cc. of concentrated sulphuric acid. For the next operation the parts J, L, M are kept assembled.

(2) *Determination of Mercury in Absence of Iodine*

If the substance analyzed contains iodine, the procedure described in (3) is used.

Preparation of Distillate for Precipitation—The contents of the parts I, J, K are transferred to the flask L in the following manner. The receiver L is surrounded by ice-water, and the sulphuric acid in J is allowed to enter *one drop at a time,* regulated by the stopcock Q. This operation must be conducted with much care, as the introduction of the strong sulphuric acid causes vigorous evolution of hydrogen chloride. If the parts J, L, M are kept assembled during the transfer, the flask L externally cooled, and the sulphuric acid introduced as directed, the process is easily controlled and there is no loss of mercury.

The condenser-tube, reservoir J, etc., are disconnected from the flask L, and washed out with minimum quantity of warm water from a wash-bottle. Any resistant lumps of mercuric salt are dislodged by directing against them a stream of 3N hydrochloric acid from a wash-bottle. The contents of the trap are also transferred to the flask. The total volume of the solution at this point should be not over 80 cc.

A small square of litmus paper is added to the acid liquid, which is cooled externally, while 50% sodium hydroxide solution is added slowly from a pipette until the reaction is neutral or barely alkaline. The solution is acidified by addition of 3 cc. of concentrated hydrochloric acid. If the odor of sulphur dioxide is noticeable, the vapors from the mouth of a bromine bottle are allowed to fall into the flask until a faint yellow tinge in the liquid shows an excess of bromine.

Any slight excess of bromine thus introduced, or present after decomposition of a bromine compound, is at once reduced upon addition of the thiocyanate reagent. The liquid, which must not exceed a volume of 100 cc. is now ready for precipitation of the mercury.

Precipitation of Mercuric Zinc Thiocyanate—There is added 25 cc. of the stronger Jamieson reagent, the flask is rotated to mix its contents, and is allowed to stand for about one hour. The precipitate of mercuric zinc thiocyanate separates promptly and is at first bulky. (A red color is due to iron in the alkali used). The precipitate is filtered, with gentle suction, on a 9 cm. paper (Munktell No. 2 was used) supported by a platinum cone. The precipitating flask is cleaned out by rubbing with a policeman and by rinsing with some of the filtrate. It is finally washed out with the prepared wash-liquid (2 cc. of precipitant in 450 cc. water), and the filter paper and precipitate are washed 5 or 6 times with the same liquid.

Titration—The filter is folded and removed from the funnel, the latter being wiped with the paper to obtain any trace of precipitate which may be found on the glass. The filter paper is put into a 250 cc. iodine-flask (or glass-stoppered Erlenmeyer), treated with 45 cc. of the cold hydrochloric acid reagent (1 part water, 3.5 parts concentrated hydrochloric acid), and 6-7 cc. of chloroform added. The liquid is at once titrated with the standard iodate solution, with continual agitation of the flask. Upon addition of iodate, the color at first deepens, and then fades. When most of the color is gone, the flask is stoppered and shaken, a violet coloration of the chloroform indicating iodine not yet converted into iodine chloride. The addition of the iodate in small portions is continued, with frequent shaking of the stoppered flask, until the last faint tint in the chloroform is just discharged. The end-point is excellent.

Results for organic mercury compounds are given in Table VIII.

Tests to Determine Completeness of Distillation and Accuracy of Procedure as Described.

Results of the final tests to determine the completeness of the anhydrous distillation, and of the retention of mercury in the receiver, are shown below. Samples of purified mercuric chloride were used, and the procedure described was modified only by omission of the ammonium persulphate.

$HgCl_2$ gm.	Hg taken gm.	Hg found gm.	Error gm.
0.1479	0.1092	0.1094	+0.0002
0.1249	0.0922	0.0920	−0.0002
0.1363	0.1006	0.1006	0.0000
0.0997	0.0736	0.0736	0.0000

Qualitative tests of the acid residue in the decomposition flask after distillation showed mercury to be absent in every case.

(3) *Determination of Mercury in Presence of Iodine*

Most of the iodine distills over as such during the decomposition, and before the mercury begins to volatilize in quantity. The formation of mercuric iodide in the receivers makes it necessary to wash them out with potassium iodide solution. The mercury is then present as potassium mercuric iodide, and cannot be precipitated by Jamieson's reagent. The mercury is, therefore, first isolated by addition of zinc-dust, excess zinc dissolved by hydrochloric acid, the residual mercury dissolved in nitric acid and precipitated by Jamieson's original method. The details of the procedure follow.

Procedure—

The acid-chamber J is emptied into the flask L, as described in the first paragraph of (2), page 30. The condenser-tube, reservoir J, etc., are then washed free from mercury salt with small quantities of 10% potassium iodide solution, using in all about 20 cc. The washing is completed with a little water, and the contents of the trap also transferred to the flask. The volume of the solution should be 60-70 cc.

One gram of zinc dust is suspended in a little water and added in portions to the mercury solution, which is agitated meanwhile. The analysis is allowed to stand about 2 hours, to allow excess zinc to dissolve. All the mercury is precipitated on the residual zinc. The liquid is decanted through a filter, the mercury-zinc sponge washed with water by decantation, the filter paper washed with water, and any particles of amalgamated zinc on the filter washed back into the flask. (The filter is reserved for later use). About 25 cc. of 6N hydrochloric acid is poured over the zinc and mercury sponge, and the covered flask heated for 2-3 hours nearly to the boiling-point of the liquid. Most of the zinc dissolves, leaving a globule of mercury which still contains considerable zinc. The acid liquid is decanted through the original filter paper, and the globule of mercury washed by decantation. The flask is now placed under the filter, and 5 cc. of warm concentrated nitric acid is poured carefully through the paper, in such a way as to wet its entire surface and dissolve any particles of amalgamated zinc which may be present. The filter is washed with a little water, and the mercury solution treated with bromine-water until colored and then heated until free from bromine and oxides of nitrogen.

The liquid is cooled and a small square of litmus paper is introduced. The liquid is neutralized with 50% sodium hydroxide solution, and then acidified with 3 cc. of hydrochloric acid. The volume at this point should be about 50 cc. The cooled solution is treated with 25 cc. of Jamieson's reagent (reagent A), agitated after a few minutes, and allowed to stand 1-2 hours.

The analysis is completed as described in Section 2, page 31. Results by this procedure are given in the table.

Analytical Results—

Table VIII presents results obtained with a number of organic mercury compounds of various types by the distillation method described above, and comparative results obtained by White's method (umpire method). For Table VIII see the following page.

Comments—

The agreement of results by the two methods is satisfactory. With the exception of mercurated aniline, the results by White's method are either the same as, or slightly lower than, those by the distillation method. It has already been pointed out (page 25) that White's method, as here performed, may be affected by a slight loss of mercury during the decomposition, and hence sometimes yields results a little too low.

The compounds analyzed varied widely in purity. Mercury-p-ditolyl and mercuric cyanide were quite pure, while the butyl mercaptide was much contaminated with chlorine, and the mercurated o-nitrotoluene was apparently in large part mercuric oxide. The results in all cases show the effectiveness of the persulphate-sulphuric acid decomposition, as applied to mercury derivatives of organic compounds of varied types: hydrocarbon, phenol, phthalein, amine, mercaptan, nitro-compound and cyanide.

The presence of bromine is shown to introduce no difficulty, and the modified procedure was successful in determining satisfactorily the mercury in presence of iodine.

The use of *potassium dichromate* (or chromium trioxide) and sulphuric acid for the decomposition, as first intended, was found to be inadmissible. The decomposition itself was satisfactory, but it was impossible to distill out mercury chloride completely in a current of hydrogen chloride, even at 320° C. for 30 minutes, retention by the precipitated anhydrous chromic sulphate appearing to occur. It may be noted that Fischer[29] observed a similar effect of large amounts of ferrous chloride upon the volatilization of mercuric chloride by the wet method.

The use of *ammonium persulphate and concentrated sulphuric acid* for analytical destructive oxidation of organic compounds is apparently new, though several workers have used persulphate under other conditions. Newberry[37] used ammonium persulphate and

TABLE VIII

RESULTS OF ANALYSIS OF SOME TYPICAL ORGANIC COMPOUNDS OF MERCURY

Compound	Distillation Method		Hg found by Umpire Method %	Remarks
	Sample gm.	Hg found %		
Mercury p–ditolyl Theoretical Hg = 52.42%	0.2077 0.2090	52.42 52.30 Av. 52.36	51.92 51.85 Av. 51.89	
Diacetatomercuriphenol	0.1508 0.1537	66.36 66.40 Av. 66.38	66.43 66.29 Av. 66.36	
n–Butyl mercaptide[40]	0.2000 0.2206	61.14 61.06 Av. 61.10		Contained much Cl. Not analyzable by KSCN titration
Tetrahydroxymercury fluorescein (Na salt)[41]	0.3048 0.3045	31.23 31.19 Av. 31.21	30.63 30.66 Av. 30.65	
Dibromo-hydroxymercury fluorescein[42]	0.3576 0.3543 0.3599	27.89 27.71 27.71 Av. 27.77	27.87* 27.66* Av. 27.77	*Determined as sulphide
p–Aminophenylmercuricacetate	0.2009 0.2055	59.78 59.84 Av. 59.81	60.05 60.06 Av. 60.06	
Mercurated o–nitrotoluene[43]	0.1311 0.1363	89.66 89.74 Av. 89.70	89.32 89.49 Av. 89.41	
Mercuric cyanide Theoretical Hg = 79.41%	0.1534	79.34	79.44 79.35 Av. 79.39	
Dibromofluorescein and diacetatomercuriphenol (mixture)	0.1514	66.12	66.36	Mixture contained 0.10 gm. of the halogen compound
Diiodofluorescein and diacetatomercuriphenol (mixture)	0.1505	66.35	66.36	Mixture contained 0.10 gm. of the halogen compound

water in decomposing organic compounds to be analyzed for arsenic. Duret[38] used the same oxidant with 10% sulphuric acid in decomposing the organic matter of urine preparatory to determination of mercury. Rupp and Lehmann[35] and Meyer[39] used potassium persulphate and dilute sulphuric acid for decomposition of organic arsenic compounds, but found action of permanganate and sulphuric acid to be better.

The persulphate-sulphuric acid decomposition, described above, possesses several marked advantages over other methods in common use. The oxidation is smooth and rapid, but not violent. It occurs at relatively low temperatures (e.g., around 100° C.). Excess persulphate is easily reduced on heating and the reduction-product, ammonium (potassium) bisulphate, is not likely to interfere with subsequent operations. Evolution of sulphur dioxide or of ozone might, of course, interfere with analyses other than that for mercury.

III—Conclusions

(1) The determination of mercury as sulphide, precipitated from acid solutions by hydrogen sulphide, is affected by a considerable positive error, larger in presence of other salts and not eliminated by certain changes in procedure.

(2) In absence of halogen, decomposition of organic matter by the permanganate-sulphuric acid procedure described by White, followed by titration of mercury by thiocyanate, is a rapid and satisfactory analysis.

(3) A new general method is described for determination of mercury in organic compounds. The sample is oxidatively decomposed by persulphate and sulphuric acid, and mercury is distilled out under anhydrous conditions by passing a stream of hydrogen chloride and by heating to about 305° C. After suitable preparation of the distillate, mercury is precipitated as zinc mercuric thiocyanate and determined volumetrically by Jamieson's iodate titration.

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